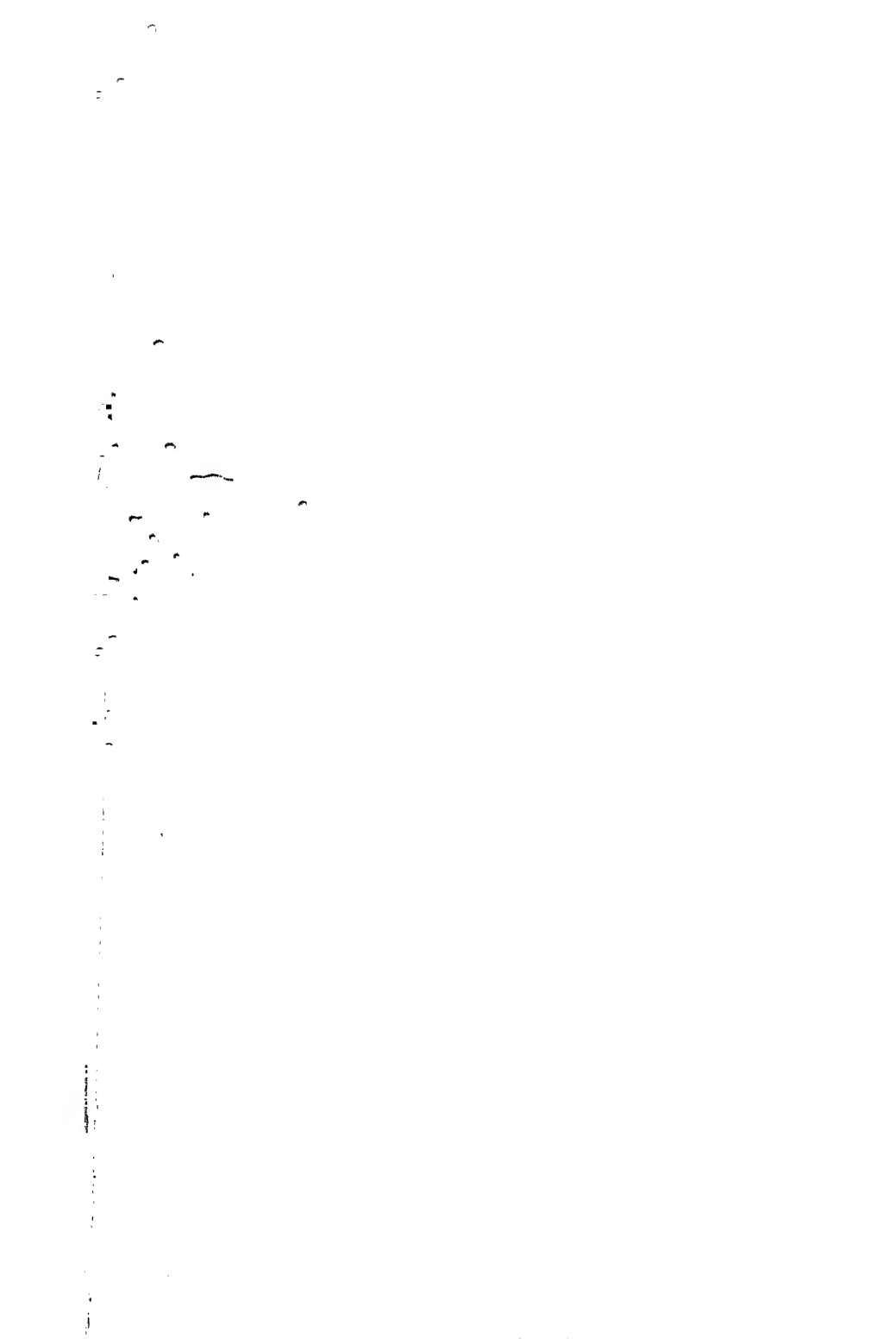


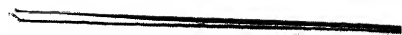
THERMODYNAMICS OF
TECHNICAL GAS-REACTIONS





THERMODYNAMICS OF
TECHNICAL GAS-REACTIONS





THERMODYNAMICS OF TECHNICAL GAS-REACTIONS

SEVEN LECTURES

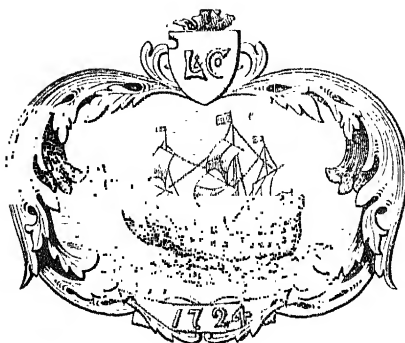
BY
DR. F. HABER

Ö. PROFESSOR AT THE TECHNISCHE HOCHSCHULE, CARLSRUHE

TRANSLATED BY
ARTHUR B. LAMB, PH.D.

DIRECTOR OF THE HAVEMEYER CHEMICAL LABORATORY,
NEW YORK UNIVERSITY, NEW YORK CITY

WITH 20 FIGURES



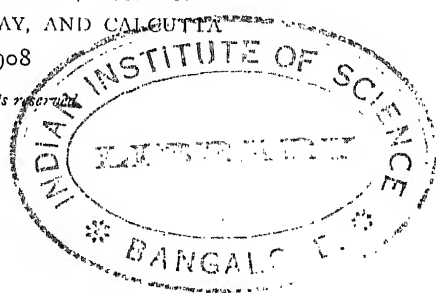
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TO
MY DEAR WIFE
CLARA HABER, Ph.D.,
IN GRATITUDE FOR HER SILENT CO-OPERATION

TRANSLATOR'S PREFACE

THE fascinating possibility of predicting the course of a chemical reaction from a few characteristic constants of the reacting substances seemed very far from realization after the ill-starred attempt of Berthelot. Recent attacks upon this problem have been more successful, and the future is promising.

Prof. Haber's book entitled "Thermodynamik Technischer Gasreactionen" is a most important contribution to this subject. It is a pleasure for me to assist in making this book better known to the English-speaking world.

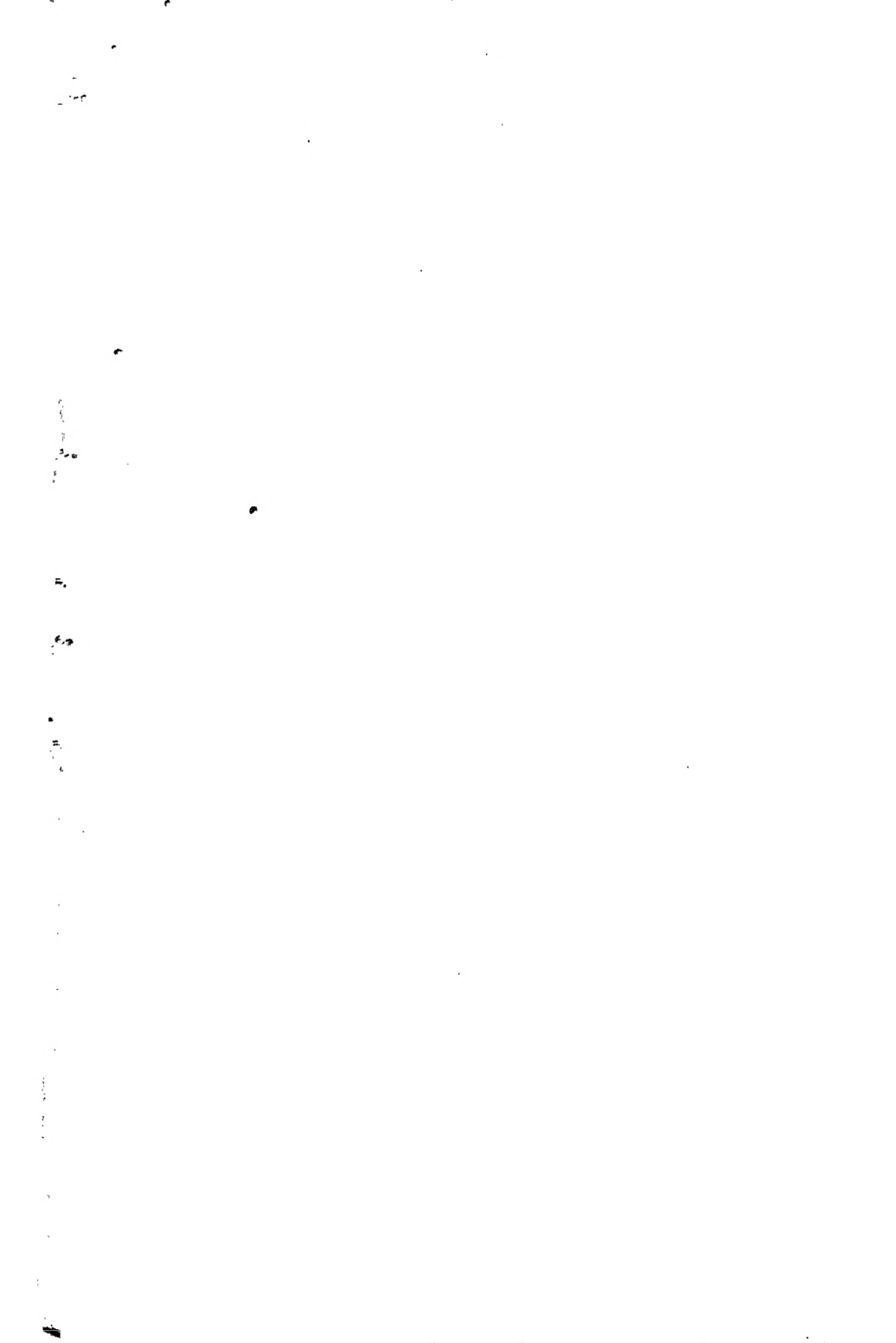
Professor Haber has thoroughly revised the German edition purposely for this translation. Many parts have been re-written, and the changes necessitated by the progress of the subject during the years 1905 and 1906 have been made. In those lectures where this involved too extensive alterations the original text has been adhered to, and the new results added in appendices. The appendix to the Third Lecture was translated by Dr. Maitland, that to the Fifth by Mr. R. Le Rossignol.

The translation of the first four Lectures was completed in its final form in the spring of 1906.

It gives me pleasure to acknowledge the valuable assistance rendered me by Dr. M. H. Hunter in the reading of the proofs.

ARTHUR B. LAMB.

NEW YORK CITY,
October 1st, 1907.



P R E F A C E

DURING February of this year I delivered a series of seven evening lectures on the thermodynamics of technical gas reactions, before several of my colleagues and a number of my younger research students. I could assume that my audience was familiar with the chemical and technical side of the subject, but was obliged to develop the mechanical theory of heat from its very foundations. These lectures, intended simply to introduce the subject for discussion by my colleagues and students, are here reproduced.

Questions asked me after the lectures, and certain difficulties which were encountered in making the subject clear, have led me to make my explanations here somewhat fuller, and to adopt the style of an essay rather than of a lecture.

I have not made use of the atomic hypothesis in these lectures. This is not due to any antagonism on my part to this hypothesis. I am simply convinced that the application of the mechanical theory of heat to chemistry becomes easier and more comprehensible the closer we restrict ourselves to the heat and work effects of masses directly perceptible to our senses.

In presenting the fundamentals of this theory, I have chosen Helmholtz's point of view. From it a chemical reaction is considered to have a latent heat just as does any simple change in the state of aggregation. Consequently, in my presentation, the two parts into which total energy can be divided are not spoken of as *free* and *bound energy*, but as *reaction energy* and *latent heat*. Various reasons have led me to adopt this less usual nomenclature. In the first place, latent heat is a concrete entity appealing directly to our senses. The idea of "bound energy" is an abstraction. Then, too, the intimate theoretical

and practical connection between gas reactions and the dissociation and vaporization of solids can be much more readily appreciated from this standpoint. Finally, starting from it, there is no difficulty in grasping both the idea of a temperature coefficient of maximum work, upon which van't Hoff, Ostwald, and Nernst based certain special considerations, and the idea of entropy which underlies Planck's method of treatment.

In connection with the work of Helmholtz, and particularly because of an article by van't Hoff in the "Festschrift" published in celebration of Boltzmann's sixtieth birthday, I have discussed at length the influence of specific heats on the energy of gaseous reactions. The *special* importance of specific heats in this kind of reactions is fully discussed at the end of the Fourth Lecture. The methods of measuring specific heats, and the data we thus far possess in this field, have also been treated at length; indeed, very much at length in some places, in order to permit the reader to criticize the choice finally made. Our knowledge of specific heats is at present so scanty that we must often trust to a sort of expert instinct in selecting proper values, without being able in some instances to prove definitely that the chosen results are really better than those of some other investigator.

The book has been written for the sake of technical rather than theoretical chemistry. I hope that it may facilitate both teaching and experimental investigation of the subject of technical gas reactions. It is not a handbook, nor does it attempt a complete presentation of all the material, but rather a clear and exhaustive treatment of the more important cases. How well I have succeeded in this clarification must be left to the decision of my colleagues.

Messrs. Gottlob and Moser have assisted me greatly in the many numerical computations contained in the book. I shall be grateful for notification of any inaccuracies of any kind which may be found.

F. HABER.

CARLSRUHE,
May 20th, 1905.

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UNIT OF S...

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THERMODYNAMICS

FIRST LECTURE

THE LATENT HEAT OF CHEMICAL REACTION AND ITS RELATION TO REACTION ENERGY

GENTLEMEN,—In these lectures I shall endeavour to make clear the significance of heat factors in gas reactions, with especial reference to the specific heats of the interacting substances and to the heat evolved during the reaction.

Thermochemistry concerns itself in general with the total amount of heat evolved (or absorbed) during the whole course of a reaction, but leaves quite untouched the question as to whether the reaction goes to completion in one direction or halts in an intermediate (equilibrium) condition.

All simple gas reactions do halt at such equilibrium conditions, and are consequently incomplete. Often, indeed as a rule, this incompleteness only becomes perceptible at high temperatures.¹ But phenomena at high temperatures are precisely what interest us here. In the region of low temperatures, gases often react very sluggishly with one another. The reaction velocities are then the governing factors of the process, and these are not to be predicted in advance from the standpoint of the theory of heat. The higher the temperature rises the less important do these factors become, while the equilibrium phenomena which are subject to theoretical treatment attain prominence. These equilibrium phenomena² are all that we shall concern ourselves with here.

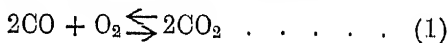
¹ Theoretically every reaction belongs to this class, and may therefore be termed reversible. But it must be possible to demonstrate experimentally this reversibility under any conditions if its theoretical consideration is to be scientifically useful.

² Here we mean only "real" equilibria, which can be reached from both sides. The "false" equilibria, which can be reached from one side only, and their relation to passive resistance and reaction velocity, will be discussed in the last lecture.

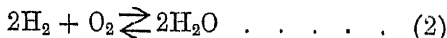
They have often been discussed in relation to the mass action of the reacting substances, but the influence exerted by the specific heat of the substances has received but little attention. Le Chatelier,¹ to be sure, showed long ago, in a comprehensive work on dissociation, the importance of specific heats, but this work was not accorded the general notice which it deserved. The result is that our knowledge of the subject is limited and the number of cases at our disposal is scanty. The subject has, however, so broad a significance that it is well worth our while to become conversant with it. Only when we consider the joint effect of mass action and the specific heats of the reacting substances are we able, from observations made at any one temperature, to draw inferences regarding the phenomena which will take place at a temperature, say a thousand degrees higher. The theory even affords us the expectation of being able to find out all about a gas equilibrium at high temperatures, simply from a knowledge of the heat factors concerned, without any experimental determinations of mass actions.² Satisfactory confirmation, however, of this last step is lacking, because our knowledge of the specific heats of gases is as yet too incomplete.

Technical
interest
of gas
reactions
at high
tempera-
tures.

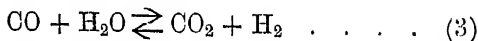
Gas reactions at high temperatures frequently possess a very great practical interest. We should mention, in the first place, those heating processes where carbon dioxide and water vapour are formed. These substances dissociate at very high temperatures into free oxygen, carbon monoxide, and hydrogen. The effect of temperature and the composition of the gas mixture on the dissociation of the carbon dioxide and the water-vapour is a first question of importance, which must be solved by means of the mechanical theory of heat. The two reactions—



and



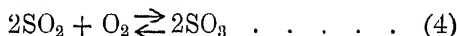
are connected with one another by the relation—



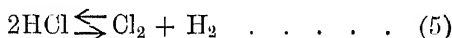
¹ *Annales des Mines*, viii. 13 (1888), 157.

² Since the publication of the German edition of this book, Nerust has given his views on this problem. See his "Thermodynamics and Chemistry" (Chas. Scribner's Sons, New York, 1907). An account of them will be found at the end of the Third Lecture.

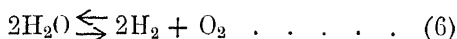
We can decide in which direction this so-called "water-gas reaction" will proceed at a given concentration of the four substances in the gas mixture, and at a known high temperature, when the dissociation conditions represented in (1) and (2) are known. Dissociation of this kind also possesses a great significance in technical inorganic chemistry. The reaction—



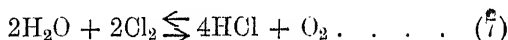
forms, as is well known, the foundation of the modern method of sulphuric acid manufacture. The two reactions—



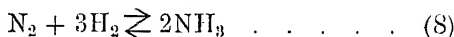
and



taken together, give us Deacon's chlorine process—



The possibility of making ammonia from its elements, and nitric oxide, and consequently nitric acid and the nitrates, from the air, is governed by the relationships given by the mechanical theory of heat for the reactions—



and



The fundamental thermodynamic relations which we will consider can be applied to the reactions of solids, liquids, and gases. They are employed under the most varied forms, especially for molten and dissolved substances. But they assume a particularly simple form for gaseous substances, because in these the pressure, temperature, and volume are connected by a very simple relation, while in the case of molten or dissolved substances no similar general relation connecting these three quantities is known. This relation is—

$$pv = RT \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where p = pressure and v = volume. If we consider a mol as the unit of mass, experiment shows us that at a pressure of one atmosphere (*i.e.* at 760 mm. Hg at sea-level and latitude 45°) this unit of mass occupies 22·412 litres at a temperature of 0°. Equation (10) requires that the temperature be reckoned in

degrees on the absolute scale. The zero point of this scale is generally put at -273°C . It is equal to minus the reciprocal value of the coefficient of expansion of an ideal gas ($\frac{1}{273}$). The coefficients of ordinary gases are very slightly different from this. By careful consideration of the deviation from the behaviour of ideal gases which ordinary gases show on compression and expansion it is possible to find the coefficient of expansion of ideal gases.¹ It amounts to $\frac{1}{273.09}$. The absolute zero therefore is, strictly speaking, not at -273°C ., but 0.09° lower.² This difference will be too small to be considered in our later calculations, but we must take account of it here, in order to determine R with all possible precision. We then get—

The gas
constant
in litre-
atmo-
spheres.

$$\frac{22.412 \times 1}{273.09} = 0.08207$$

This value of R is expressed in litre \times atmosphere units (litre-atmospheres). If we compute the volume in cubic centimetres and the pressure in dynes per square centimetres, it becomes—

The gas
constant
in absolute
units.

$$R = \frac{22,412 \times 76 \times 13.596 \times 980.6}{273.09} = 0.83155 \times 10^8 \text{ abs. units } \left(\frac{\text{erg}}{\text{T}} \right)$$

Here 76 is the height in centimetres of a column of mercury which exerts a pressure of one atmosphere; 13.596 the weight in grams of a cubic centimetre Hg; and therefore 76×13.596 the weight of the mercury column which exerts a pressure of one atmosphere per square centimetre. Since the gram weight at sea-level and lat. 45° corresponds to 980.6 dynes, then $76 \times 13.596 \times 980.6$ is the pressure in absolute measure of an atmosphere on a unit of surface (1 sq. cm.); that is, the pressure on a piston 1 sq. cm. in area working in a cylinder containing 1 mol (22,412 c.c.) of gas.

For our purposes it is most convenient to measure R in heat units (gram calories). We therefore need to know the value of a gram calorie in absolute units.

¹ For the theory see Mach, "Prinzipien der Wärmelehre" (1900), 2nd edit., p. 309 (or translation).

² Daniel Berthelot, *Z. f. Electrochemie*, x. (1904), 621; and Nernst, *idem.*, 629.

This value depends upon the temperature at which it is determined. At present it is usual to define a calorie as that quantity of heat which will warm 1 gram water from 15° to 16°.¹ The quantity of heat required to raise 1 gram of water from 0° to 1° is greater than this by 0.06 per cent. This somewhat larger zero-point calorie used to be (till about 1880) preferred. In its stead Schuller and Wartha² substituted the quantity of heat necessary to heat 0.01 gram of water from 0° to 100°. (Ostwald³ took a hundred times this value as a unit and called it K.) This "mean calorie" is very nearly equal to the 15° calorie.⁴ The mechanical equivalent of heat has been set by the Committee on Units of the Deutschen Bunsengesellschaft as equal to 41.89×10^6 erg.⁵

We get from this—

$$R = \frac{0.83155 \times 10^8}{41.89 \times 10^6} = 1.98507 \left(\frac{\text{gram-cal.}}{T} \right) \quad \text{The gas constant in heat units.}$$

We shall use later, in our numerical calculations, the abbreviated value 1.98, which is very near the exact value of R computed on the basis of the 15° calorie, the zero-point calorie, and the mean calorie.

The reactions (1) to (9) all proceed till they reach an equilibrium. Indeed, the characteristic of the equilibrium condition is that there the reaction will not of itself spontaneously progress in either the one or the other direction. That is, the driving force of a chemical reaction is zero at the equilibrium point. If we know the composition of the gas mixture at equilibrium for any given temperature, then for any other composition of the gas mixture at the same temperature the driving force of the reaction is given by the *distance from the equilibrium point*.

We should at first be inclined to call the reaction energy

¹ Or more accurately from 15½° to 16½°. Compare Warburg's report on the unit of heat read before the Naturforscherversammlung in Munich (1899, "Bericht über die Verhandlungen," p. 62).

² *Wied. Ann.*, 2 (1877), 365.

³ *Lehrb. d. allg. Chemie*, II₂ (Leipzig, 1893), p. 72.

⁴ According to Behn (Drude's *Ann.*, 16 (1905), 653), the mean calorie is greater by 0.03 per cent., according to Dieterici (*idem.*, p. 593), 0.2 per cent. greater, than the 15° calorie. Other figures are given by Planck ("Thermodynamik" (Leipzig, 1905), 2nd edit., p. 31).

⁵ *Zeitschr. f. Elektrochemie*, ix. (1903) 686.

the total work which a chemical reaction can do during its whole course. This definition, however, is unsuitable for theoretical treatment.

Reaction
energy
and com-
position.

The driving force of a chemical reaction changes continuously with the changing composition of the reacting mixture. The nearer we approach the equilibrium point where the reaction stops, the smaller does this driving force become. We take as units of transformation, the transformation of such amounts as appear in equations (1) to (9). Thus, in reaction (2), the change of one mol O_2 , two mols H_2 , into two mols H_2O is the unit of transformation. The reaction energy of every infinitely small fraction dx of this unit quantity is equal to the driving force A multiplied by the quantity transformed, that is $A \times dx$. To get the total energy of transformation, we must find the sum of all the quantities $A \times dx$ with the aid of the integral calculus, having first expressed A as a function of x . Such an expression would be awkward and involved. It is therefore better to consider the quantity of gas so great that the transformation of a unit quantity would have no appreciable effect on the composition of the mixture, and consequently cause no appreciable change in its driving force. We then get for the product of the driving force into the unit quantity transformed (that is, one mol) the value $A \times 1 = A$, and consider this as the reaction energy. The value A of the reaction energy, therefore, characterizes only a single tiny phase in the progress of the reaction, during which the composition remains constant. It shows us, however, how far we are from the end of the reaction or the equilibrium point where $A = \text{zero}$, and this is the important thing.

Measure
of reaction
energy.

The reaction energy A may be expressed in any units of energy which suit our convenience. In what follows, we shall always measure it in gram calories, taking for practical reasons as far as possible the 15° calorie as our unit of heat. However, the older data are often expressed without any precise definition of the calorie used, and the possibility even of a sure recalculation is not always afforded by the data given. The smallness of the difference between the mean, the zero and the 15° calorie makes this uncertainty less troublesome.

How com-
position

Considering the composition of the gas as invariable during the reaction, we are at liberty to express this composition either